3D printed mixed flow reactor for geochemical rate measurements

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ABSTRACT

Desktop 3D printing is a rapid, low-cost, and flexible method for fabricating chemical reactors for low temperature geochemical investigations and engineering tests. Reactor designs can be easily shared between research groups. Here we demonstrate how a mixed flow reactor (MFR) designed to measure mineral precipitation rates is fabricated by desktop additive manufacturing (3D printing). Models of the MFR top and base were created by computer-aided design software and used to generate stereolithography input files. These files were converted to physical models using stereolithography (SLA) 3D printing technology. Comparison of the model input files to actual prototypes showed that the manufactured reactor parts matched the model as closely as machined parts match mechanical drawings. Although this reactor was designed to measure mineral precipitation rates, it can be easily modified for use in mineral dissolution experiments. The reactor can also be used to synthesize large quantities of solids from a solution with a fixed composition and be combined with *in situ* scattering and spectroscopic methods for real time studies of mineral growth/dissolution processes.

1. Introduction

Slow reaction rates allow many Earth surface and near surface geochemical processes to persist in a state of disequilibrium. That means that models of those processes that are based on the local equilibrium assumption can be quite inaccurate. This problem can be resolved by incorporating geochemical kinetics principles and data into the models. However, in spite of more than 30 years of rate measurements, geochemical rate data are comparatively sparse and considerably less reliable than available thermodynamic data. This lack of rate data impedes scientific investigations of important geochemical processes, such as chemical weathering and early diagenesis, and technological analyses of important environmental and industrial processes, such as CO_2 sequestration, mine waste remediation, and high-level radioactive waste disposal. In order to remedy this problem we need rate measurement methods that are rapid, low-cost, and easily adaptable to a wide range of reaction types.

Rate measurement experiments are done in three types of reactors: batch reactors (BR), mixed flow reactors (MFR), and plug flow reactors (PFR) (see chapter 4 in Rimstidt, 2014). Batch and plug flow reactors are easy to design and operate but they produce concentration versus time data that must be differentiated to obtain reaction rates. By comparison mixed flow reactors are more complicated to construct but they have the advantage of measuring rates directly without the need for the error-magnifying differentiation step. MFR reaction rates are

found by multiplying the difference in the concentration of the rate determining species between the feed and discharged solution by the flow rate (e.g. Rimstidt and Dove, 1986).

In addition to being inexpensive, adaptable, and easily manufactured, MFRs should have several other features. Most importantly the MFR must be well mixed so that the effluent solution is a perfect sample of the reactor contents. That allows the measured reaction rate to be correlated directly to the solution chemistry without a need for buffers or back-calculation of solution compositions. Furthermore, the mixing speed should be adjustable so that the operator can test for, and eliminate, transport limited reaction rates. The reactor should have multiple inlets, each independently fed by a pump with an adjustable flow rate to allow the operator to easily change the solution composition in the reactor. This makes it possible to obtain multiple rate measurements over ranges of solution composition for each set up. The reactor should be able to contain solid samples that react with the solution. The reactors should also have a small internal volume so they will respond quickly to changes in feed solution composition, flow rate, or reaction rate. Transparent reactors are desirable because they allow the operator to monitor the stirring process by means of dye injections. Finally, the reactors should be unreactive, leak proof, easily cleaned, easy to assemble, and thermally stable.

Reactors meeting these design criteria can be produced from acrylic (or similar) plastics by a slow and expensive machining process. Here, we describe an alternative manufacturing process that produces reactor

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bodies quickly and cost-effectively using desktop 3D printing. While machining typically takes a few weeks to complete, with each reactor costing several hundreds of dollars, our 3D printed reactors can be produced in a matter of days at a much lower cost.

The potential of 3D printing in fabricating reactionware has grown significantly in recent years in large part because of the availability of relatively inexpensive and easy-to-use 3D printers. The focus of studies using 3D printing for this purpose has largely been in the field of microfluidics. Au et al. (2016) recently published a thorough review paper describing the current state of 3D printing technology for microfluidics. The review highlights the advantages of stereolithography such as increased affordability, resolution, and design flexibility. They also predicted that the future of microfluidics will be dominated by stereolithography printing with designs available online, although it has been pointed out that some barriers remain in terms of resolution, cost, and, in certain applications, biocompatibility (Waheed et al., 2016). Fortunately, issues related to resolution are significantly less important for MFRs and other types of reactors having relatively large internal features that are typically millimeter-scale or larger. Biocompatibility is also not an issue for inorganic precipitation/dissolution experiments like those described here. Thus, the combination of desktop SLA 3D printing technologies with mixed flow reactor devices for precipitation/dissolution experiments has the potential to significantly advance the current state of experimental techniques in geochemical kinetics with implications for understanding contaminant transport, biogeochemical cycling, as well as the formation of aqueous nanomaterials.

2. Stereolithography

We use inverse stereolithography (SLA) desktop 3D printing to manufacture reactors because it produces final printed parts with optimal porosity, permeability, surface roughness, resolution, and optical characteristics. Although production-grade stereolithography printers are expensive, desktop versions are a suitable and cost-effective alternative that deliver high quality printed parts. Fused filament fabrication (FFF) also known as fused deposition modeling (FDM) is another popular 3D printing method. Generally speaking, parts fabricated by FFF have higher porosity, permeability, and surface roughness than SLA and therefore are less well suited for MFR fabrication. Transparent filaments are now commercially available for 3D printing purposes; however, the optical clarity of the printed parts is significantly lower when compared to parts printed with the SLA method, and coatings of epoxy or enamel are thus required to better seal and improve their optical properties.

Stereolithography builds a 3D model layer-by-layer by hardening a liquid photopolymer (resin) using a laser beam. Fig. 1A shows the main parts of a SLA printer. It consists of a blue 405 nm laser, one or more mirrors along the optical path that direct and position the laser beam, a resin tank with an optically transparent window at the bottom that allows the laser light to pass, and a build platform attached to a motorized elevator. A UV-filtering enclosure prevents the photopolymer resin from curing prematurely due to exposure to ambient light. At the start of each new print, the build platform lowers into the tank displacing the resin and stops a fixed distance from the tank bottom. This distance, typically tens to hundreds of micrometers, is entirely filled with a liquid resin film (Fig. 1B). The laser beam sweeps repeatedly across the build platform in a pattern that corresponds to the area of the first layer of the part. The light polymerizes the resin into a solid form. After the scan is complete the build platform rises and the newly formed solid layer is released from the bottom of the resin tank. The build platform lowers into the resin tank again and a new liquid resin film is created between the first solid layer and the base of the resin tank. The layer formation process repeats hundreds to thousands of times until the part is complete (Fig. 1C). Parts can be printed with or without supports (Fig. 1D) and any necessary supports are removed during post processing. Stereolithography (SLA) has been described in detail previously (e.g., Bártolo, 2011).

We used a Formlabs Form 2 printer to print the reactors described in this paper because of the feature and layer resolution, choice of resins, modest cost (~3500 USD), and previous experience with an earlier Form 1+ model. The Form 2 has a maximum build volume of 145 × 145 × 175 mm (5.7 × 5.7 x 6.9 in). The laser spot size (full-width-at-half-maximum, FWHM) is 140 μm (0.0055 in) and a 25, 50, or 100 μm (0.001, 0.002, and 0.004 in) layer thicknesses can be specified. The spot size and layer thickness settings of the printer determine the minimum dimension of a part in the X/Y and Z directions, respectively. The Form 2 printer uses a Class 1, 250 mW 405 nm violet laser. The resin and tank are heated during printing to maintain an optimal temperature. Desktop SLA and digital light processing (DLP) printers with similar features and resin choices are also available from other manufactures (e.g., 3D systems, DWS, Flashforge).

The parts described in this study were printed using a layer thickness of 50 μm and the standard transparent resin (V2-FLGPCL02) distributed by Formlabs. As reported by the manufacturer, the resin is a proprietary mixture of methacrylated monomers and oligomers with a photoinitiator. Other resin options are available with different colors (e.g., black, grey, white), and different formulations (e.g., Tough, Durable, Flexible, High Temp) that simulate a range of injection-molded plastics. The manufacturer has reported selected bulk
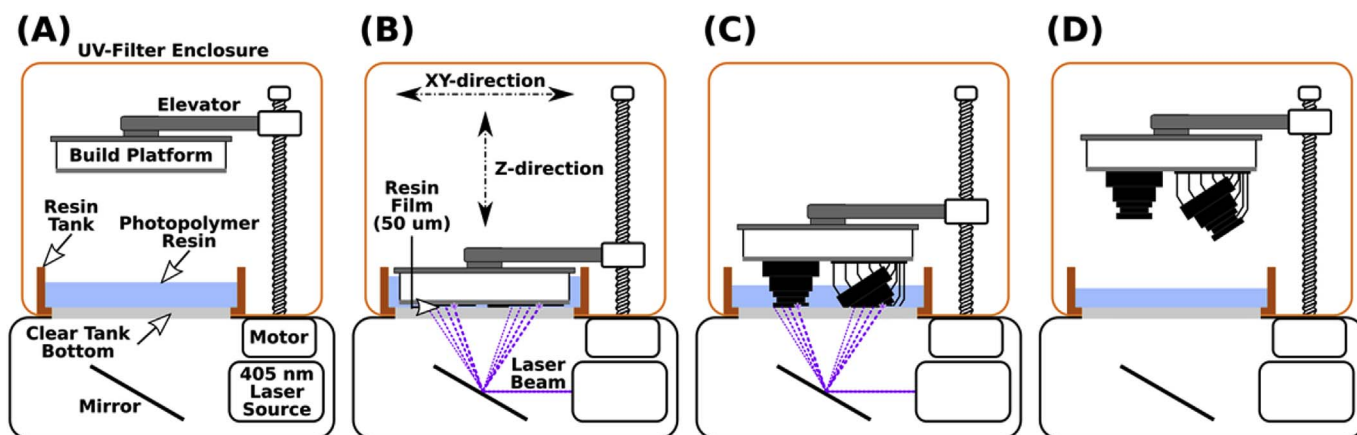

Fig. 1. The basic parts and operations of a desktop (inverse) stereolithography printer similar to the Formlabs Form 2 used to manufacture the reactor described in this paper. (A) At the beginning of a new print a motorized elevator lowers the build platform into the resin tank creating a thin film of resin between it and the base of the resin tank. (B) The laser shines through the clear tank bottom and polymerizes the photopolymer resin layer. (C) It scans in the X/Y-direction creating the first solid layer of the part (left) or the base of the support structure (right). The parts adhere to the build platform and are printed layer-by-layer in the Z-direction until the fabrication is complete. (D) The example shows a MFR top printed with (right) and without supports (left).